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Inês Coutinho, Teresa Medici, Robert Wiley, Luís Cerqueira Alves, Bernard Gratuze, and Márcia Vilarigues

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SEVERAL recent archaeological excavations in Portugal have revealed large quantities of glass objects dated from the late medieval to early modern periods. Many of them have forms that are common among European finds, but there is one particular form that frequently appears only in Portugal. Vessels of this form, shown in Figure 1, are called gourds (*cabaças* in Portuguese and *calabashes* in English) because they resemble these plants of the Cucurbitaceae family (*Lagenaria siceraria*). A previous study of this form concluded that these vessels were common glass containers in Portugal during the 17th and 18th centuries.[1]

The Form

This peculiar form is characterized by a neck that can be globular, pear-shaped, or truncated conical, while the body is usually globular.[2] The rim can be outfolded or simply cut off and finished with an applied trail. The latter kind of rim is documented in Portugal from the 15th century on, and it appears to have become popular during the 17th century.[3]

The body of the gourd is globular and usually decorated with vertical ribs made by using a dip mold, starting from the bottom of the neck.[4] Many of the gourds discovered to date are of brownish red, green (several shades can be observed), or blue glass. Less often, colorless glass gourds have been found, some of them with a greenish or yellowish tinge. The smaller gourds (H. about 10.0 cm or less) were mainly blown, but no mold-blown decoration has so far been identified. Instead, these gourds were decorated with the millefiori or pick-up technique, sometimes associated with the presence of gold leaf applied with heat.[5]

Comparing the gourd-shaped bottles with the vegetable gourds shown in Figure 1 demonstrates that some of the former—including fragments SCV-V177, SCV-V352, SCV-V390, SJT0128, and SCV-V022, reproduced in an archaeological drawing—were made in a direct attempt to imitate the latter. On the other hand, fragments SCV-V079, SCV-V082, SCV-V115, SCV-V210, SCV-V365, and SCV-V423 present a more stylized shape based on the vegetable gourd, but with visual differences, such as the vertical ribs on the body and the truncated conical neck.

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1. Teresa Medici and others, "Glass Bottles and Jugs from the Monastery of Sta. Clara-a-Velha, Coimbra, Portugal," *Annales de l'Association Internationale pour l'Histoire du Verre*, v. 17, Antwerp, 2006 (2009), pp. 391–400; Teresa Medici, "Vidros da Terra. O vidro tardomedieval e moderno em Portugal (séc. XIV–XVII). O contributo da arqueologia," Ph.D. diss., Universidade de Coimbra, 2014, p. 274.
2. Medici and others [note 1].
3. Teresa Medici, "The Glass Finds from Rua da Judiaria, Almada, Portugal (12th–19th Century)," *Revista Portuguesa de Arqueologia*, v. 8, no. 2, 2005, pp. 535–569; Medici and others [note 1]; Medici [note1], p. 271.
4. Medici and others [note 1]; Medici [note 1], p. 271.
5. *Ibid.*

FIG. 1. *Fragments of gourds from the assemblage formed from excavations at the monasteries of Santa Clara-a-Velha (Coimbra) and São João de Tarouca, with an archaeological drawing illustrating the shape of a complete gourd-shaped bottle, and two vegetable gourds.*

Manufacturing Technique

Because of the complexity of the form, the techniques by which the gourds were manufactured were not fully understood until replicas were made. The master glass artist Robert Wiley conducted some experiments at the research unit VICARTE (Vidro e Cerâmica para as Artes) at the Universidade NOVA de Lisboa in Caparica, Portugal. He demonstrated that the gourds were formed by a two-step post-gather process (Fig. 2). The first gather was collected from the crucible of molten glass in the furnace, blown, and worked with the jacks, thus forming the neck (post) of the gourd. When the neck had attained its final shape, a second gather was added over the lower portion of the post. This second gather was then lowered into a dip mold and blown to become imprinted with the ribbed pattern. The post was removed from the mold, and the glass was blown again to form the body of the gourd. A pontil was attached to the bottom of the gourd and the blowpipe was removed, permitting the lip to be finished with the jacks. The object was then placed in an annealing chamber.[6]

The experiment suggested that the original glassmakers exercised considerable control over temperature while employing the Venetian technique of *mezza-stampatura* (half-molding).

6. Medici [note 1], pp. 271–272.

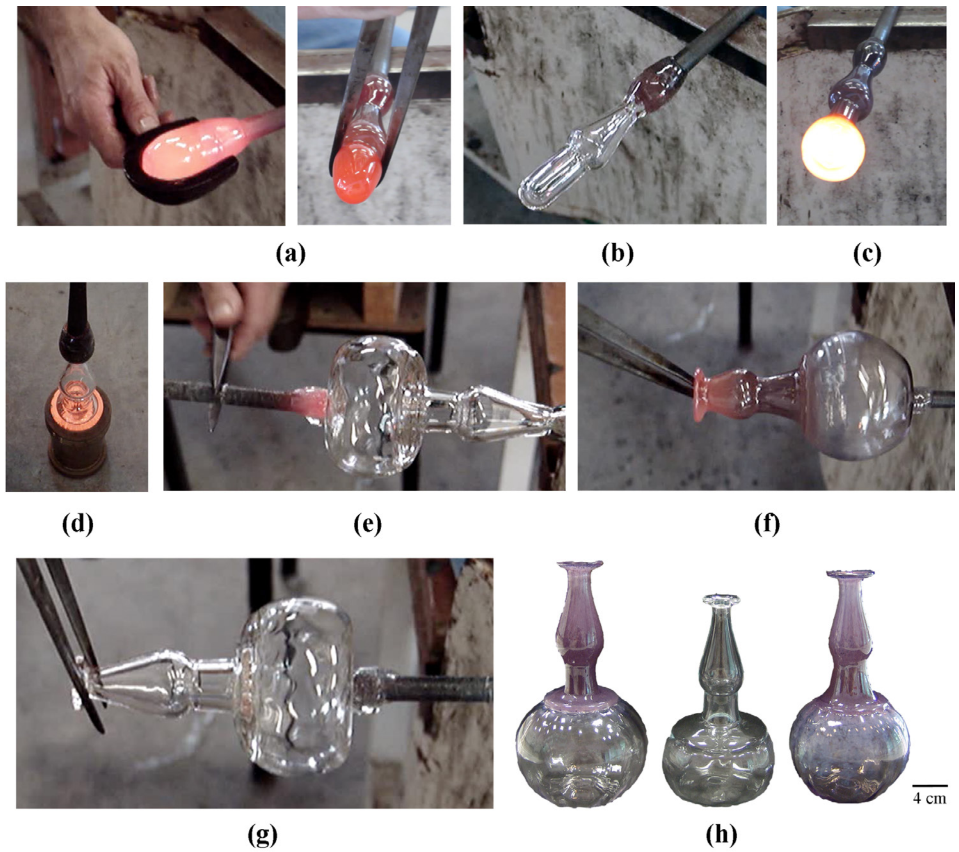

FIG. 2. *Steps in making a gourd: (a) a bubble is worked with jacks to (b) shape the neck (post); (c) a second gather is added to the neck and (d) blown into a mold to obtain a ribbed pattern; the glass is blown again to shape the globular body of the gourd; (e) the pontil is attached to the bottom of the gourd, and the blowpipe is removed from the neck; (f) the lip is worked with the jacks; and (g) the neck is elongated. Some examples of the gourds obtained during this experiment are shown in (h).*

Other techniques and production technologies may have been employed in making the gourd-shaped vessels, but this seems to have been the most probable method.

The Gourd in Europe and the Iberian Peninsula

Gourd-shaped bottles were probably very common in Portugal from the 17th century onward. The entry for *cabaça* in a dictionary published in Coimbra at the beginning of the 18th century expressly mentions the existence of glass vases with this form: "CABAÇA. Especie de abobara. . . . Vaso da casca do fruto, que tem o mesmo nome. . . . Cabaça também se chama qualquer vaso de vidro, ou de outra matéria–de figura semelhante à de aquelle fructo."[7] Glass

7. "CABAÇA. Sort of gourd. . . . Vessel made from the skin of the fruit of the same name. . . . Also called cabaça is any vessel made of glass, or of other materials, of a shape similar to that fruit." Author's translation from Rafael Bluteau, *Vocabulario portuguez e latino, aulico, anatomico, architectonico* . . . , 10 vv., Collegio das Artes da Companhia de Jesu, Coimbra, 1712–1728, v. 2, letter "C," pp. 3–4. Digital copy of the Biblioteca Nacional de Portugal, http://purl.pt/13969 (accessed August 15, 2016).

bottles of this form have been found in archaeological assemblages at São João de Tarouca, Porto, Coimbra, Santarém, Lisbon, Almada, and Moura, all of them dated to the 17th century, demonstrating that this form was widely disseminated throughout the country.[8]

Elsewhere on the Iberian Peninsula, gourd-shaped glass vessels are found in Spain, especially in the territories that belonged to the Kingdom of Aragon. They are mentioned in several inventories in Catalonia (15th century) and Majorca (16th century).[9] Gourds found in Catalonia were made of thick dark glass or thin colorless glass, and they were employed in pharmaceutical and domestic contexts.[10] They are characterized by a globular neck very similar to, but smaller than, the body. A good example of such a gourd-shaped vessel can be seen in the Museo del Castillo de Peralada in Girona.

Despite their rare occurrence outside the Iberian Peninsula, some gourd-shaped vessels can be found among 16th-century Venetian and *façon de Venise* glasses produced mainly in chalcedony glass. One example is now in the Museum of Decorative Arts in Prague.[11]

French examples include gourds attributed to Bernard Perrot, the well-known Italian glassmaker who was active in Orléans, France, in the late 17th and early 18th centuries.[12] These gourds are made of tinned glass and usually have a metallic stopper. During the 18th century, bottles in the form of gourds and covered in wicker ("gourds/bottles of the shepherd," called, in French, *gourdes/bouteilles de berger*), were common in the region of Provence. Such vessels were used, principally by shepherds and fishermen, until the end of the 19th century.[13] Two gourds recovered from archaeological excavations in France are worth noting here. One was unearthed in the Louvre excavations in Paris, and it is dated to the second half of the 16th century.[14] The other gourd, from the "dépotoir de l'hôpital de la Charité," was found in the Place Antonin Poncet in Lyon, and it is dated between 1677 and 1680. The latter was designated as an alembic.[15]

None of the examples of gourds mentioned above matches the forms of the gourds discovered in Portugal. When comparing gourds found in Portugal with those discovered elsewhere in Europe, certain morphological differences can be detected. The Portuguese gourds have a pear-shaped or truncated conical neck, as was described above and is illustrated in Figure 1. These neck shapes contrast with the most commonly globular necks in the gourds found in Spain and other European countries.

A painting by the famous 17th-century Portuguese painter Josefa de Ayala e Cabrera (also known as Josefa de Óbidos, 1630–1684) depicts a gourd-shaped bottle of colorless glass, with an outline that matches the gourds with a

8. Medici [note 1], pp. 278–285.

9. José María Gudiol Ricart, *Els vidres catalans*, Monumenta Cataloniae, v. 3, Barcelona: Ed. Alpha, 1936, p. 41; Miquel Àngel Capellà Galmés, *Ars vitraria: Mallorca (1300–1700)*, Palma: Edicions UIB, 2015, p. 182.

10. Carme Prats i Darder, *Apotecaria de Santa Maria de Vallbona*, Santes Creus: Fundació d'Historia i Art Roger de Belfort, 1990; Josep Antoni Cerdà i Mellado, "El conjunt de vidre mataroní trobat a les excavacions de la Plaça Gran de Mataró (1982)," *Laietania*, no. 11, 1998, pp. 163–200, esp. pp. 180–181; Jean-Paul Philippart and Markus Mergenthaler, eds., *Frágil transparencia: Vidrios españoles de los siglos XVI a XVIII*, Dettelbach, Germany: Verlag J. H. Röll GmbH, 2011, p. 119, no. 27.

11. Karel Hetteš and Jiřina Vydrová, *Benátské sklo = Vetro veneziano = Venetian Glass*, Prague: Uměleckoprůmyslové Muzeum v Praze, 1973, cat. no. 179, fig. 45.

12. *Bernard Perrot (1640–1709): Secrets et chefs-d'oeuvre des verreries royales d'Orléans*, Orléans: Musée des Beaux-Arts d'Orléans, and Paris: Somogy, 2010, p. 122, nos. 35 and 36.

13. Jacqueline Bellanger, *Verre d'usage et de prestige: France, 1500–1800*, Paris: Editions de l'Amateur, 1988, pp. 380–381.

14. Danièle Foy and Geneviève Sennequier, eds., *À travers le verre: Du Moyen Âge à la Renaissance*, Rouen: Musées et Monuments Départementaux de la Seine-Maritime, 1989, p. 314 and colorplate XXI, cat. no. 343.

15. Michelle Auger, "Verrerie," in Christine Becker and others, "Fouille de la Place Antonin Poncet à Lyon," *Archéologie du Midi Médiéval*, v. 7, 1989, p. 184, fig. 37.29.

FIG. 3. *Painting by Josefa de Ayala e Cabrera depicting a gourd-shaped vessel in glass.* Nature morte avec plat en argent, bourse d'écus, boîte, terre cuite et vase de fleurs*, about 1670. Private collection (Vitor Serrão and Pierre-Nicolas Sainte-Fare-Garnot,* Rouge et or: Trésors du Portugal baroque*, [Portugal]: Gabinete das Relações Internacionais, 2001, pp. 140–141).*

truncated conical neck (Fig. 3). This is the closest representation to the vessels discussed in this article.

Function of the Gourd

The lack of archaeological evidence on the function of these bottles prompted an investigation of written and iconographic sources.

It is commonly accepted that these gourds were made to contain liquids. Portuguese documents of the 12th, 13th, and 15th centuries mention the use of gourds, in their vegetable form, as wine containers; this seems to be confirmed by their appearance in medieval sculptures depicting Christian pilgrims.[16]

In the painting by Josefa de Óbidos mentioned above, the gourd-shaped bottle, decorated with pink ribbons and stopped with a piece of twisted paper or a cloth, seems to be filled with a colorless liquid. It may contain rose water or a liqueur.

In certain paintings, gourds are associated with medicine, although it is unclear whether they were made of glass. One example is *São Cosme e São Damião*, dated to the second quarter of the 16th century and now in the Museu Nacional Machado de Castro (MNMC 2540). The gourd-shaped bottle depicted in this painting is different in some respects from the bottles we studied. This gourd has a globular body with an S-shaped ribbed pattern. The globular neck was formed before the lip.

One cannot help wondering if larger gourds, in which the neck is so developed that it seems to be almost a second container, were shaped in this way to serve solely an ornamental purpose.

The smaller gourds were probably used as perfume bottles. According to Manuela Almeida Ferreira, the gourd could be related to the *qumqum*, a vessel for perfumed water that was very

16. Medici [note 1], p. 276; Begoña Farré Torras, "Do apóstolo ao peregrino: A iconografia de São Tiago na escultura devocional medieval em Portugal," *Medievalista*, no. 12, July–December 2012, www.fcsh.unl.pt/iem/medievalista/MEDIEVALISTA12/torras1204.html (accessed June 23, 2016).

common among Islamic glasses, suggesting that this form may date back to the period of Arab rule.[17] Bottles of this form were still being produced at the Marinha Grande Royal Glass Factory during the 19th century, and they appeared in the factory's catalog.[18]

ARCHAEOMETRIC INVESTIGATION

Because of its unique nature and its restricted presence in Portugal, we consider the gourds to offer a potentially very important case study for enriching our current knowledge about the circulation and production of glass in that country. A further investigation was thus conducted, combining a stylistic approach and chemical characterization, which was intended to suggest the provenance and manufacturing techniques of these objects.

Archaeological Contexts

We selected 10 gourd-shaped bottles from two archaeological assemblages: nine from the Monastery of Santa Clara-a-Velha (SCV) in Coimbra were sampled and analyzed by μ-PIXE and LA-ICP-MS, and one gourd from the Monastery of São João de Tarouca (SJT) was sampled and analyzed by μ-PIXE (see Figure 1). The results from both techniques were compared. Similar comparisons have been discussed elsewhere.[19]

Monastery of Santa Clara-a-Velha. This monastery belonged to the Poor Clares (Order of Saint Clare), a contemplative order of nuns in the Roman Catholic Church. The order, founded in 1212 and named after the abbess Clara Offreduccio de Favarone (about 1193–1253), was inspired by the Franciscan ideal of renouncing the possession of goods, which was seen as the means of achieving individual purification and the remission of society's sins. All goods were supposed to be held by the community, while the nuns themselves should live in absolute poverty. During the following centuries, most of the young women who joined the Poor Clares in the monastery enjoyed a high social status, and they were probably members of noble families, judging from their family names and the high quality of the objects retrieved from the excavation.[20] Investigations of post-medieval and early modern European monastic environments have shown a disparity between the rules and real-life practices.[21]

The location of the monastery, which is situated close to the Mondego River, resulted in regular flooding. This prompted the decision to construct a new monastery (Santa Clara-a-Nova) on a nearby hill, some distance from the riverbank. Construction began in 1649, using some materials from the old monastery. By 1672, some members of the religious order had abandoned the old building, and five years later, the grave of the founder, Elizabeth of Portugal (1270–1334), was moved from the old monastery to the new one. The old monastery remained abandoned and was partly submerged until 1995, when archaeological intervention was initiated. That intervention, which lasted until 2000, was initially directed by the Instituto de Arqueologia da Faculdade de Letras da Universidade de Coimbra and then transferred to the monastery itself (it was promoted to a dependent service of the Instituto Português do Património Arquitectónico, IPPAR). The monastery's rehabilitation program ended in 2009; in that year, the Museum of the Santa Clara-a-Velha Monastery opened on the site, just in front

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17. Manuela Almeida Ferreira, "Espólio vítreo proveniente de estação arqueológica do Mosteiro de Sta. Clara-a-Velha de Coimbra: Resultados preliminares," *Revista Portuguesa de Arqueologia*, v. 7, no. 2, 2004, pp. 541–583.

18. Jorge Custódio, *A Real Fábrica de Vidros de Coina (1719–1747) e o vidro em Portugal nos séculos XVII e XVIII: Aspectos históricos, tecnológicos, artísticos e arqueológicos*, Lisbon: Instituto Português do Património Arquitectónico, 2002, p. 57.

19. Inês Coutinho and others, "Provenance Studies on Façon-de-Venise Glass Excavated in Portugal," *Journal of Archaeological Science: Reports*, v. 7, 2016, pp. 437–448.

20. Sara Dias Trindade and Lígia Inês Gambini, *Mosteiro de Santa Clara de Coimbra: Do convento à ruína, da ruína à contemporaneidade*, 2nd ed., [Coimbra]: Direcção Regional de Cultura do Centro, 2009, pp. 13, 14, and 26.

21. See, for example, Silvia Evangelisti, *Nuns: A History of Convent Life, 1450–1700*, Oxford, U.K., and New York: Oxford University Press, 2007, pp. 28–29.

of the monastery itself, displaying objects that had been housed in the monastery.[22]

During the archaeological work, some objects and materials were found, including the graves of several nuns. Among the objects were common and glazed ceramic objects, some of which were decorated with coats of arms, as well as high-quality Chinese porcelain and such metal utensils as spindles, needles, thimbles, and scissors. Other finds were made of jet and glass. With the human remains were several gold wires used to attach teeth, another demonstration of the high social status of some of the monastery's residents. The monastery itself was profusely decorated with Hispano-Moresque ceramic tiles[23] and limestone statues.[24]

Monastery of São João de Tarouca. Tarouca is located in northern Portugal, and the monastery was founded between 1152 and 1154. It is believed to be the earliest Cistercian monastery in that country.[25]

In the Cistercian order, a new monastery had to be linked to or affiliated with an existing one in a sort of mother–daughter relationship. São João de Tarouca, which was tied to the Clairvaux Abbey in Ville-sous-la-Ferté, France, flourished during the 12th and 13th centuries. It was, in turn, responsible for the founding of the monasteries of Santa Maria de Fiães, São Pedro das Águias, and Santa Maria de Aguiar. It was later replaced by the Santa Maria de Alcobaça abbey.[26]

The Monastery of São João de Tarouca followed Cistercian guidelines in regard to its architecture and construction. The buildings are devoid of decoration and marked by straight lines. Poverty and simplicity were its most cherished principles, resulting in the absence of mural paintings, stained glass panels, and bell towers. The monastery was built in a perfect Cistercian geographical location: near two watercourses, with fertile lands and in total isolation.[27]

During the 16th century, the monastery reached its apogee from an economic and social perspective. This lasted until 1834, when all of the religious orders were extinct. During the period of prosperity, the ideals of poverty, simplicity, and an absence of material goods no longer applied in the daily life of the Cistercian monks.[28] This is indicated by the number and quality of the ceramic and glass finds retrieved from the monastery. The excavations were conducted by IPPAR from 1998 to 2001.

Analytical Studies

Samples. Small (0.2–0.4 cm^2) samples from broken objects and on individual fragments without possible connections were dry-cut from the glass fragments with a diamond wire. The samples were embedded in an epoxy resin and polished with SiC sandpaper down to 4000 mesh.

μ-PIXE. Quantitative results were achieved with the μ-PIXE ion beam analytical technique, using an Oxford Microbeams OM150 scanning nuclear microprobe with an in-vacuum or external beam configuration. To permit the efficient detection of low-energy X-rays, such as those of sodium, all of the glass fragments were irradiated in-vacuum with a focused 1 MeV proton beam. The X-rays were collected by an 8-μm-thick beryllium windowed silicon drift detector (SDD) with 145 eV resolution. To avoid or detect possible local glass heterogeneities, X-ray imaging (2D elemental distribution) and spectra were obtained from an irradiated sample area of 750 x 750 μm^2.

For the quantification of trace elements (typically elements with an atomic number above

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22. Trindade and Gambini [note 20], pp. 65–80.
23. Susana Coentro and others, "Hispano-Moresque Ceramic Tiles from the Monastery of Santa Clara-a-Velha (Coimbra, Portugal)," *Journal of Archaeological Science*, v. 41, January 2014, pp. 21–28.
24. Trindade and Gambini [note 20], pp. 40–47.
25. Ana Sampaio Castro and Luís Sebastian, "A componente de desenho cerâmico na intervenção arqueológica no Mosteiro de S. João de Tarouca, 1998–2001," *Património/Estudos*, v. 2, 2002, pp. 33–42.
26. *Ibid.*
27. *Ibid.*
28. *Ibid.*; Ana Sampaio Castro and Luís Sebastian, "Mosteiro de S. João de Tarouca: 700 anos de história da cerâmica," *Património/Estudos*, v. 3, 2002, pp. 165–177.

TABLE 1

Chemical Compositions of the Glass Samples Analyzed by μ-PIXE, Presented in Weight Percent of Oxides (wt %)

	Glass Color	*Na_2O*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*Cl*	*K_2O*	*CaO*
SCV-V079	Green	19.9	5.6	6.8	55.5	0.45	0.03	0.86	2.08	6.67
SCV-V082	Purple (reddish)	15.0	4.8	4.8	64.0	0.43	0.02	0.74	2.36	5.09
SCV-V115	Light blue	17.6	3.1	2.3	66.5	0.09	0.07	0.76	2.53	6.07
SCV-V177	Yellow	18.9	4.2	7.7	55.3	0.18	0.04	0.56	4.32	7.40
SCV-V210	Turquoise blue	18.3	2.9	1.4	62.9	0.26	0.24	0.69	2.12	5.58
SCV-V352	Olive green	20.6	5.5	7.7	56.7	0.33	0.02	0.91	1.77	3.26
SCV-V365	Green	18.6	6.1	6.1	60.8	0.35	0.06	1.00	1.43	3.22
SCV-V390	Green (brownish)	16.4	6.6	9.2	54.2	0.73	0.03	0.78	1.89	5.03
SCV-V423	Light blue	16.9	6.6	9.2	54.3	0.73	0.02	0.82	1.85	4.85
SJT0128	Green	17.2	6.9	6.5	58.0	0.54	0.02	0.88	1.51	6.10
SCV-V191	(*Façon de Venise*)	16.3	2.5	1.2	67.7	< 0.12	0.10	0.69	3.79	6.62
SCV-V193	(*Façon de Venise*)	18.1	2.8	0.8	68.0	0.13	0.10	0.61	2.47	5.91
SCV-V195	(*Façon de Venise*)	18.0	2.7	0.8	68.3	0.11	0.10	0.65	2.39	5.68
SCV-V408 *	(*Façon de Venise*)	11.5	3.5	1.5	64.0	0.19	n.m.***	0.84	5.46	11.9
Corning B										
Measured by μ-PIXE		15.5	0.9	4.3	64.6	0.46	—	—	1.05	8.48
Certified Value**		17.0	1.03	4.36	62.27	0.34	—	—	1.00	8.56
Corning A										
Measured by LA-ICP-MS		13.5	2.4	0.9	68.0	0.11	—	—	2.85	5.39
Certified Value**		14.3	2.66	1.00	67.03	0.13	—	—	2.87	5.03

* The composition of this fragment (SCV-V408) was obtained only by means of LA-ICP-MS.

** Certified values for the CMoG standards taken from R.H. Brill, *Chemical Analyses of Early Glasses*, v. 2, *Tables of Analyses*, Corning: The Corning Museum of Glass, 1999, p. 544.

*** n.m. = not measured

that of iron), higher energy was required, and so a 2 MeV proton beam was used. In this case, the external beam setup was chosen to prevent sample-beam charging and consequently X-ray spectra degradation. X-rays were collected with an SDD with 145 eV resolution from a sample area of 800 x 800 μm^2. Operation and basic data manipulation, including elemental distribution mapping, was achieved through the OMDAQ software,[29] and quantitative analysis employed the GUPIX program.[30]

29. G. W. Grime and M. Dawson, "Recent Developments in Data Acquisition and Processing on the Oxford Scanning Proton Microprobe," *Nuclear Instruments & Methods in Physics Research, Section B, Beam Interactions with Materials and Atoms*, v. 104, nos. 1–4, 1995, pp. 107–113.

30. J. L. Campbell and others, "The Guelph PIXE Software Package IV," *Nuclear Instruments and Methods B*, v. 268, no. 20, 2010, pp. 3356–3363.

TiO_2	*MnO*	*Fe_2O_3*	*CoO*	*NiO*	*CuO*	*ZnO*	*As_2O_3*	*SrO*	*BaO*	*PbO*
0.28	0.35	1.26	< 60 µg/g	30 µg/g	50 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 20 µg/g
0.23	1.22	0.94	< 40 µg/g	20 µg/g	0.01	0.01	< 10 µg/g	0.02	0.04	< 10 µg/g
0.09	0.02	0.64	< 30 µg/g	< 10 µg/g	< 10 µg/g	50 µg/g	< 10 µg/g	0.06	< 0.01	0.01
0.17	0.58	0.59	< 30 µg/g	< 10 µg/g	30 µg/g	60 µg/g	< 10 µg/g	0.04	0.04	< 30 µg/g
0.04	0.46	0.39	70 µg/g	50 µg/g	0.94	60 µg/g	< 20 µg/g	0.02	0.01	1.89
0.31	1.13	1.66	< 0.01	20 µg/g	60 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 30 µg/g
0.31	0.43	1.26	< 20 µg/g	30 µg/g	30 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 10 µg/g
0.36	2.08	2.37	< 20 µg/g	40 µg/g	0.02	0.01	0.01	0.03	0.04	< 0.01
0.34	1.93	2.25	0.01	30 µg/g	0.02	0.01	< 50 µg/g	0.03	0.04	< 30 µg/g
0.24	0.06	1.87	0.01	20 µg/g	< 10 µg/g	60 µg/g	< 70 µg/g	0.03	< 0.04	< 40 µg/g
0.06	0.31	0.38	< 20 µg/g	< 10 µg/g	40 µg/g	40 µg/g	< 20 µg/g	0.03	n.m.	0.03
0.03	0.38	0.33	< 20 µg/g	30 µg/g	30 µg/g	60 µg/g	0.01	0.03	n.m.	0.03
0.04	0.45	0.39	< 25 µg/g	40 µg/g	30 µg/g	50 µg/g	< 20 µg/g	0.05	n.m.	0.03
0.07	0.34	0.61	< 10 µg/g	< 10 µg/g	20 µg/g	50 µg/g	< 10 µg/g	0.07	n.m.	10 µg/g
0.1	0.28	0.38	—	—	2.85	0.16	—	—	—	0.51
0.089	0.25	0.34	0.046	0.099	2.66	0.19	—	0.019	0.12	0.61
0.75	0.98	1.06	0.17	—	1.10	0.053	—	0.10	0.42	0.066
0.79	1.00	1.09	0.17	—	1.17	0.044	—	0.10	0.56	0.12

The results are expressed in weight percentage of oxides, normalized to 100 percent. To validate the concentration results, a glass reference standard, Corning B, was also analyzed. The values are presented in Table 1.

LA-ICP-MS. The SCV fragments were also analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) as part of a larger research project. The analysis was performed on the resin-embedded glass cross section. The ablation system employed here is located at the Centre National de la Recherche Scientifique (CNRS) in Orléans, France. It consists of a Nd:YAG laser working at 266 nm (quadrupled frequency), with a maximum energy of 2 mJ and at a maximum pulse frequency of 15 Hz. The beam diameter can be adjusted from 20 µm to 100 µm. The glass analysis was performed at 8 Hz with a beam diameter of 80 µm. A pre-ablation time of 20 s was set to eliminate the transient part of the signal, which was then acquired for 55 s, corresponding to 20

TABLE 2

Trace Elements and REE Concentration in μg/g for the SCV Samples (Gourd-Shaped Bottles and *Façon de Venise* Objects), Measured by LA-ICP-MS

	SCV-V079	*SCV-V082*	*SCV-V115*	*SCV-V177*	*SCV-V210*	*SCV-V352*	*SCV-V365*	*SCV-V390*
B	173	175	56.2	107	99.9	224	216	243
Ti	1783	1592	558	1082	307	2174	1939	2299
V	17.7	14.1	11.1	19.4	8.2	18.7	17.5	27.1
Cr	17.3	10.6	8.6	12.2	6.5	24.6	17.2	26.8
Co	4.0	6.5	1.7	3.9	52.5	8.2	4.3	9.0
Ni	11.2	11.5	4.5	6.0	40.0	16.5	11.7	17.1
Cu	24.7	52.7	9.2	21.7	8793	44.1	20.1	160
Zn	71.9	68.2	25.2	38.3	37.1	66.7	62.5	81.9
As	4.6	11.3	1.8	12.2	133.1	13.9	4.9	25.9
Rb	12.2	29.6	27.7	63.3	14.3	18.5	14.2	19.4
Sr	442	372	825	599	391	324	436	405
Y	11.2	9.7	3.3	6.6	2.9	11.4	13.7	15.1
Zr	139	128	30.6	60.1	21.1	124	193	165
Nb	4.8	4.3	1.8	3.3	1.1	5.8	5.7	6.0
Mo	0.2	0.6	0.3	0.6	1.4	0.3	0.2	0.6
Sn	8.9	16.7	6.8	9.0	18503	8.3	18.8	19.2
Sb	0.3	0.7	0.2	0.4	18.3	< dll*	0.4	3.3
Ba	189	325	69.9	325	92.9	238	217	387
La	23.4	14.5	4.9	11.2	3.4	16.3	28.4	27.0
Ce	48.5	27.5	9.0	21.2	6.3	33.1	56.4	53.8
Pr	5.3	3.1	1.0	2.3	< dll	3.5	6.3	5.9
Nd	21.4	12.3	4.0	9.4	< dll	14.0	24.5	23.4
Sm	4.0	2.4	0.8	1.9	< dll	2.7	4.5	4.5
Eu	0.6	0.4	< dll	0.4	< dll	0.5	0.5	0.6
Gd	2.8	1.8	0.4	1.5	< dll	2.2	3.3	3.4
Tb	0.4	0.3	0.1	0.2	0.1	0.3	0.5	0.5
Dy	2.2	1.7	0.6	1.3	0.5	2.1	2.6	2.7
Ho	0.5	0.4	0.1	0.2	0.1	0.4	0.5	0.6
Er	1.2	0.9	0.3	0.7	0.3	1.2	1.4	1.5
Tm	0.2	0.1	0.1	0.1	< dll	0.2	0.2	0.2
Yb	1.2	1.1	0.3	0.7	< dll	1.3	1.5	1.6
Lu	0.2	0.1	0.1	0.1	< dll	0.2	0.2	0.2
Hf	3.8	3.4	0.8	1.6	0.6	3.2	5.1	4.4
Pb	15.3	24.4	< dll	10.7	19498	13.8	25.7	21.6
Th	8.9	5.3	1.5	3.7	0.9	6.0	11.7	10.5
U	1.9	1.4	0.5	1.4	0.6	1.9	2.4	2.6

* dll = detection limits

SCV-V423	SCV-V191	SCV-V193	SCV-V195	SCV-V408
237	57.2	68.6	68.8	51.5
2317	325	197	210	408
26.8	8.4	7.5	7.4	10.1
27.4	7.4	6.7	6.9	7.0
8.9	14.9	18.9	18.5	4.0
16.8	6.6	20.2	19.4	5.3
162	27.2	35.1	35.3	13.1
81.9	22.8	33.4	34.2	40.0
25.0	9.6	34.4	34.2	4.3
19.4	18.5	13.4	13.5	21.1
408	417	427	438	588
15.2	2.6	1.6	1.7	2.9
165	21.9	9.3	10.0	25.3
6.0	1.0	0.6	0.7	1.3
0.5	0.8	1.1	1.0	1.1
17.6	274	271	277	7.5
2.1	0.3	0.4	0.4	0.8
390	296	137	138	169
27.5	3.4	1.8	1.9	4.2
55.5	6.1	3.4	3.4	8.5
6.0	0.7	0.4	0.4	0.9
23.7	2.8	1.5	1.5	3.5
4.5	0.5	0.3	0.3	0.7
0.6	< dll	< dll	< dll	0.1
3.5	0.4	0.1	0.1	0.5
0.5	0.1	0.1	0.1	0.1
3.0	0.4	0.3	0.3	0.5
0.6	0.1	0.1	0.1	0.1
1.6	0.2	0.1	0.2	0.3
0.2	< dll	< dll	< dll	< dll
1.6	0.3	0.1	0.2	0.3
0.3	0.3	< dll	< dll	< dll
4.3	0.6	0.2	0.3	0.7
19.6	252	273	389	22.8
10.6	0.9	0.4	0.5	1.2
2.7	0.3	0.5	0.5	0.8

mass scans from lithium to uranium (the signal in count/second was measured in low-resolution mode for 58 different isotopes). Calibration for glass was undertaken by using NIST610 and the Corning B, C, and D glass reference standards.[31] The detection limits range from 0.1% to 0.01% for major elements and from 20 ng/g to 500 ng/g for other elements.

The composition is calculated from the average of two ablations carried out in different areas of the sample. To validate the obtained concentration results, Corning A was analyzed; the results are presented in Table 1. The results for the trace and rare-earth elements obtained for the analyzed samples from the SCV assemblage are reported in Table 2.

UV-Vis Reflectance Spectroscopy. A MAYA 200 PRO spectrophotometer from Ocean Optics with a single-beam dispersive optic fiber was used, together with a 2048 CCD silicon detector that permits operation in the 200–1050 nm range. The light source was an HL-200-HP 20 W halogen lamp from Ocean Optics, with a single optical path between 360 and 2500 nm.

The spectra were acquired directly on the glass surface of the objects, in reflectance (R) mode, with a 45°/45° configuration (illumination angle/acquisition) and an analyzed area about 0.2 cm in diameter. Spectra were obtained between 360 and 1050 nm, with an integration time of 8 ms per scan and a total of 15 scans. A Spectralon surface was used as a reference. The obtained data were converted and presented as an absorbance $A' = \log_{10}(1/R)$. This technique is very useful for in situ analysis, being easily transportable, non-invasive, and expeditious.

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31. Bernard Gratuze, "Glass Characterisation Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry Methods," in *Modern Methods for Analysing Archaeological and Historical Glass*, v. 1, ed. Koen Janssens, Chichester, West Sussex, U.K.: Wiley, 2013, pp. 201–234; *idem*, "Application de la spectrométrie de masse à plasma avec prélèvement par ablation laser (LA-ICP-MS) à l'étude des recettes de fabrication et de la circulation des verres anciens," in Philippe Dillmann and Ludovic Bellot-Gurlet, *Circulation des matériaux et des objets dans les sociétés anciennes*, Paris: Éditions des Archives Contemporaines, 2014, pp. 259–291.

Results and Discussion

The selected samples contain 15.0–20.5 wt % sodium oxide, 54.2–66.5 wt % silica, and 1.4–4.3 wt % potassium oxide. The composition of these fragments is consistent with the use of plant ashes as the alkali source because of the relatively high contents of K_2O, MgO (2.8–6.9 wt %), and P_2O_5 (< 0.05–0.7 wt %) and the presence of chlorine.

Silica

The source of silica employed in the glass batch, usually sand, is known for containing different types of impurities.[32] Some of these impurities—such as kaolinite, feldspar, zircon ($ZrSiO_4$), monazite (REE phosphate), rutile (TiO_2), and iron oxides—are minerals that can contain various amounts of trace elements.[33] These are the main trace elements, considered trackers for sand, allowing us to consider the provenance of the raw materials and, consequently, the glass.[34]

The alumina and titanium oxide contents of the gourds were plotted (Fig. 4a), using the division in alumina content reported by Lima and others.[35] At least three different silica sources can be identified. The two gourds in the left corner of the chart (SCV-V115 and SCV-V210) have the lowest amounts of alumina, which implies the use of a purer source, or sources, of silica. The remaining gourds, which have an alumina content higher than 5 wt %, were produced using silica sources much higher in impurities. Analyzing the reported compositions of contemporaneous glass objects from such European centers as Antwerp, Amsterdam, London, and Spain (alumina values equal to or less than 2.0 wt %), we observe that alumina contents this high are unusual.[36] In glass objects from Tuscany (Gambassi and San Giovanni Valdarno), alumina contents are as much as about 4.0 wt %,[37] and in Lezhë, Albania, few samples showed values higher than 3.0 wt %.[38] The quantities of alumina in Venetian glass objects are below 2.0 wt %, even in common glass.[39] Although these values are from studies of *façon de Venise* glasses, we note them because relatively few other glasses of known provenance and similar date have been analyzed. We will not include them in our comparisons, however, because they are unrelated to the glasses discussed here.

For this reason, we decided to compare the results of our analyses of the gourds with those

32. Cesare Moretti and Sandro Hreglich, "Raw Materials, Recipes and Procedures Used for Glass Making," in *Modern Methods* [note 31], pp. 23–47.

33. *Ibid*.; Karl Hans Wedepohl, Klaus Simon, and Andreas Kronz, "The Chemical Composition Including the Rare Earth Elements of the Three Major Glass Types of Europe and the Orient Used in Late Antiquity and the Middle Ages," *Chemie der Erde–Geochemistry*, v. 71, no. 3, 2011, pp. 289–296.

34. B. Velde, "Glass Compositions over Several Millennia in the Western World," in *Modern Methods* [note 31], pp. 67–78.

35. Augusta Lima and others, "Chemical Analysis of 17th Century *Millefiori* Glasses Excavated in the Monastery of Sta. Clara-a-Velha, Portugal: Comparison with Venetian and *façon-de-Venise* Production," *Journal of Archaeological Science*, v. 39, no. 5, May 2012, pp. 1238–1248.

36. I. De Raedt and others, "Trace Analysis for Distinguishing between Venetian and Façon-de-Venise Glass Vessels of the 16th and 17th Century," *Journal of Analytical Atomic Spectrometry*, v. 16, no. 9, 2001, pp. 1012–1017; Ine De Raedt, Koen Janssens, and Johan Veeckman, "On the Distinction between 16th and 17th Century Venetian and *Façon de Venise* Glass," in *Majolica and Glass: From Italy to Antwerp and Beyond. The Transfer of Technology in the 16th–Early 17th Century*, ed. Johan Veeckman, Antwerp: [Stad Antwerpen], 2002, pp. 95–121; Stanislav Ulitzka, "Analysen von historischen Glasern – Licht im Dunkel der Geschichte?," in Anna-Elisabeth Theuerkauff-Liederwald, *Venezianisches Glas der Kunstsammlungen der Veste Coburg: Die Sammlung Herzog Alfreds von Sachsen-Coburg und Gotha (1844–1900). Venedig à la façon de Venise, Spanien, Mitteleuropa*, Lingen: Luca Verlag, 1994, pp. 40–53.

37. S. Cagno and others, "Raw Materials for Medieval to Post-Medieval Tuscan Glassmaking: New Insight from LA-ICP-MS Analyses," *Journal of Archaeological Science*, v. 37, no. 12, December 2010, pp. 3030–3036.

38. Žiga Šmit and others, "Analysis of Venetian-Type Glass Fragments from the Ancient City of Lezha (Albania)," *Nuclear Instruments & Methods in Physics Research, Section B, Beam Interactions with Materials and Atoms*, v. 267, no. 15, 2009, pp. 2538–2544.

39. Marco Verità and Sandro Zecchin, "Thousand Years of Venetian Glass: The Evolution of Chemical Composition from the Origins to the 18th Century," *Annales* [note 1], pp. 602–613.

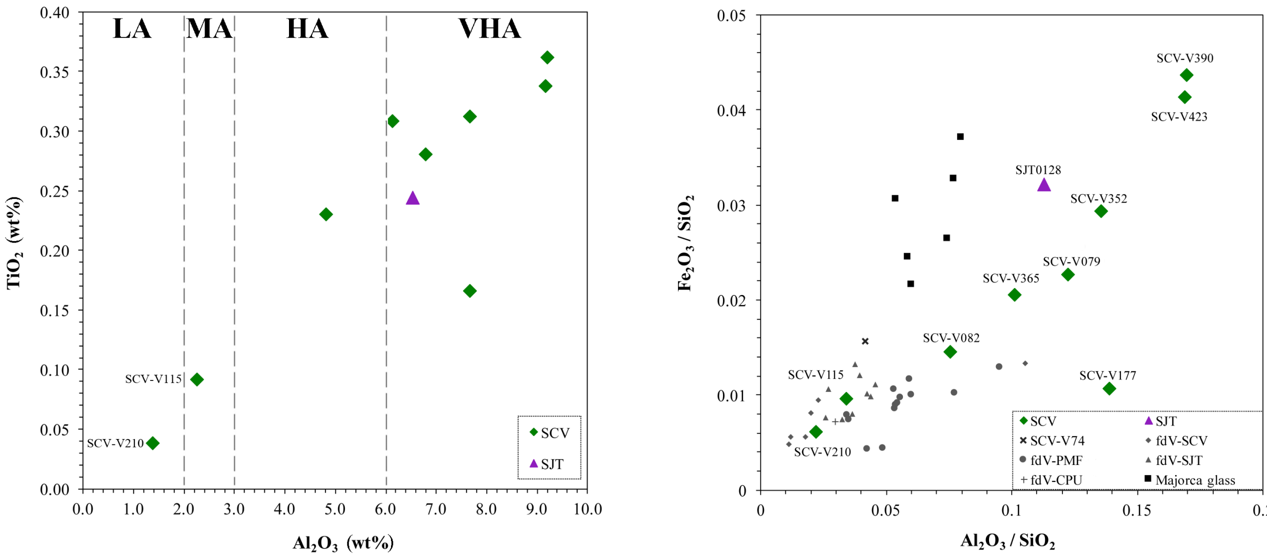


FIG. 4. *Binary plots of* (left) *alumina vs. titanium oxide, in weight percent of oxides, divided by alumina contents (LA = low alumina, MA = medium alumina, HA = high alumina, and VHA = very high alumina), following the division proposed by Lima and others [note 35], and* (right) *alumina vs. iron oxide, both normalized to the silica content and compared with another gourd from the SCV assemblage (SCV-V74, reported in Lima and others [note 35]), with results from contemporaneous* façon de Venise *objects found in Portugal (fdV, reported in Coutinho and others [note 19]), and production remains from a Majorcan furnace (Majorca glass, reported in Capellà Galmés and Albero Santacreu [note 41]). The results were obtained by μ-PIXE analysis.*

from the study of *façon de Venise* glass found in Portugal and reported by Coutinho and others.[40] These results will also be compared with data obtained for six samples of production remains recovered from a glass furnace in Majorca, Spain. The alumina values of the Majorcan samples vary between 3.5 and 5.3 wt %.[41] The composition of the body glass of a small gourd with millefiori decoration from the Monastery of Santa Clara-a-Velha, analyzed by Lima and others, will also be considered for comparison.[42]

Figure 4a shows that gourd SJT0128 is very similar to most of the SCV gourds, and they were probably made from the same source of silica. In Figure 4b, the alumina and iron oxides were normalized to the silica content to characterize the composition of the silica source, irrespective of any added flux, and plotted against each other. Again, the two gourds with lower quantities of alumina (SCV-V115 and SCV-V210) are close to each other. Five gourds from the SCV set (SCV-V079, SCV-V082, SCV-V177, SCV-V352, and SCV-V365) and the SJT gourd have an alumina to silica ratio of 0.1 to 0.15. Four of the SCV samples (SCV-V079, SCV-V082, SCV-V352, and SCV-V365) appear to be very similar, presenting a positive correlation between the alumina and iron oxides normalized to the silica contents. The closeness of the SJT gourd to the four gourds from the SCV set suggests that the same source of silica was employed to produce these glasses. The SCV-V177 gourd is outside this correlation, indicating that it was made using a different source of silica. Finally, gourds SCV-V390 and SCV-V423 were probably made from the same silica source, one very high in impurities.

40. Coutinho and others [note 19].

41. Miquel Àngel Capellà Galmés and Daniel Albero Santacreu, "El horno de vidrio del siglo XVII de Sa Gerreria (Palma, Mallorca): Contextualización histórica y análisis preliminar de los materiales," *Boletin de la Sociedad Española de Cerámica y Vidrio*, v. 54, no. 4, 2015, pp. 142–152.

42. Lima and others [note 35].

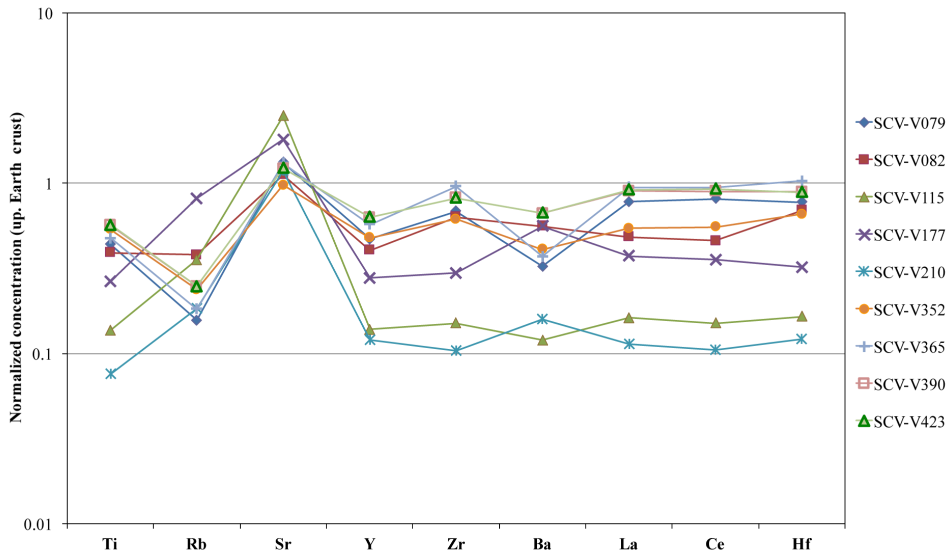


FIG. 5. *Contents of trace and rare-earth elements for SCV gourds, normalized to Earth's upper crust, in logarithmic scale.*

The gourds with high and very high alumina values are unrelated to any of the other objects. Based on their contents of oxides, the glasses from Majorca (in Figure 4b, indicated as Majorcan glass[43]) are unrelated to any of the analyzed gourds, and this demonstrates that the silica from which they were made came from a different source. Most of the analyzed *façon de Venise* fragments from the Portuguese archaeological sites of Beja (PMF) and the Monastery of São João de Tarouca (SJT) (indicated as fdV-PMF and fdV-SJT in Figure 4),[44] as well as the fragment of the small gourd SCV-V74 with millefiori decoration from the Monastery of Santa Clara-a-Velha (shown in Figure 4b),[45] do not show any similarity to the other gourds in our study, so their production, too, involved a different source of silica.

Looking at the gourds with low levels of alumina allows us to find some similarities. SCV-V210 is closely related to the three *façon de Venise* fragments from the SCV assemblage that have been identified as genuine Venetian imports.[46] SCV-V115 also seems to be similar to the *façon de Venise* fragments with low alumina contents. These similarities will be discussed below.

The rare-earth and trace elements signature for the SCV gourds is represented in Figure 5. The values were normalized to Earth's upper crust.[47] We see, for example, that fragments SCV-V390 and SCV-V423 are very similar, suggesting that they may have been made with the same source of silica and perhaps from the same batch.

These fragments are also shown in similar position in Figure 4b and in Table 1, demonstrating a close relationship in all of the quantified oxides. The coincident signature of trace and rare-earth elements, as well as the resemblance between all of the major oxides, indicates that SCV-V390 and SCV-V423 were made from the same silica source and probably in the same production center. SCV-V079 and SCV-V365, and SCV-V082 and SCV-V352, are also very similar in terms of trace and rare-earth elements, although the latter pair differ in their quantities

43. Capellà Galmés and Albero Santacreu [note 41].
44. Coutinho and others [note 19].
45. Lima and others [note 35].
46. Coutinho and others [note 19].
47. Karl Hans Wedepohl, "The Composition of the Continental Crust," *Geochimica et Cosmochimica Acta*, v. 59, no. 7, 1995, pp. 1217–1232.

of rubidium and barium. Moreover, these two fragments are related to SCV-V079, SCV-V365, SCV-V390, and SCV-V423, as can be seen in Figure 4b. Again, we can infer that this group of gourds, with high and very high alumina contents, were made from the same silica source, or from geologically related sources.

Sample SCV-V115 has the highest strontium value and lesser amounts of the other reported crust elements, which can be related to the use of a purer silica source containing strontium-bearing aragonite from seashells.[48] With its lower quantities of trace and rare-earth elements, SCV-V210 is very close to SCV-V115, again indicating the use of a purer silica source, but it does not have an equivalent elevated strontium value. Both of these gourds are plotted close together in Figure 4, and they also show lower alumina values. SCV-V210 is unique in its lead, tin, cobalt, and copper oxide values, and this composition could be attributed partly to recycled cullet, without any concern shown for the separation of colored and colorless glass.

The presence of lead and tin can be an indication that opaque glass made from lead/tin calx (used to produce the opaque white *lattimo* and present, for instance, in filigree glass) was melted together with colorless glass, and probably with some colored glasses. The presence of coloring agents such as copper oxide with a concentration of about 1 wt % can be considered a deliberate addition to the batch.

Fragment SCV-V177 has the highest rubidium and potassium oxide contents among the analyzed gourds, and its strontium value is the second highest, almost comparable to that of SCV-V115. This could indicate that its silica came from a different location. In Figure 4, this sample stands apart from the rest of the gourds, perhaps suggesting that it has a different provenance.

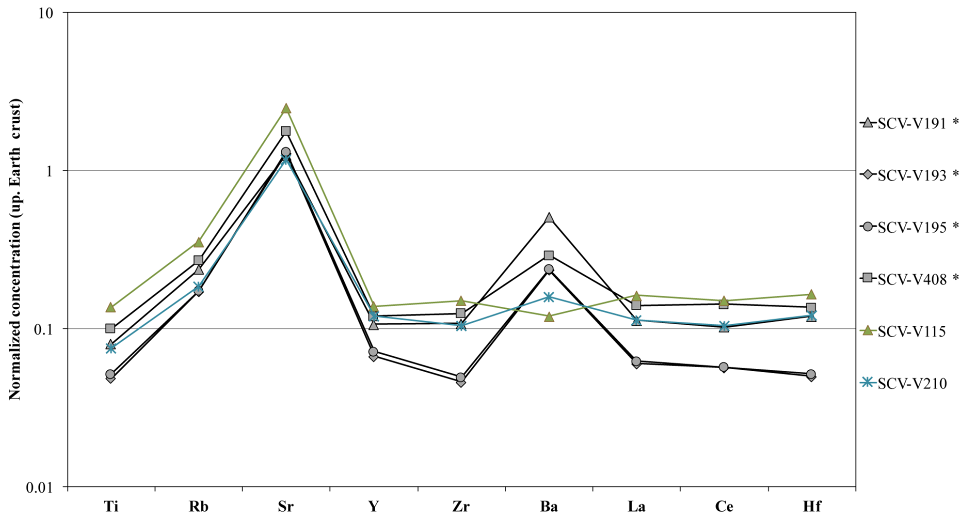
The trace- and rare-earth-element signature of the two gourds with a low content of alumina (SCV-V115 and SCV-V210) was compared with that of fragments from the Monastery of Santa Clara-a-Velha that were identified in a previous work as genuine Venetian glass imports (Fig. 6a).[49] The compositional values of the genuine Venetian objects from the SCV assemblage are presented in Tables 1 and 2.[50] Figure 6a shows a very close trace- and rare-earth-element relationship between gourd SCV-V210 and the genuine Venetian fragment SCV-V191; the major difference between them is in their barium contents. The signature of SCV-V115 is close to that of SCV-V408, but again, the levels of barium are different.

Figure 6b shows the relationship of two important elements for the provenance of silica sources: zirconium and hafnium. These elements have been very useful in distinguishing glass produced in Venice.[51] We can infer that SCV-V115 was made outside Venice. However, the silica source employed in the manufacture of this object was carefully chosen, as can be attested by the low levels of impurities in its composition. In contrast, the same figure shows that SCV-V210 is strongly compatible with Venetian glass. Because bottles of this shape are, so far, unknown among Venetian glasses, we can offer two hypotheses: (1) this object was ordered from a Venetian glass workshop in a form specified by the customer, or (2) it was made elsewhere, employing recycled Venetian glass. The second hypothesis seems more plausible, considering what was said above about the presence of lead and tin oxides in the composition of this gourd.

FLUXING AGENTS AND OTHER GLASS COMPONENTS

To compare the compositions of the gourds and contemporaneous glasses discussed elsewhere in the literature, we normalized the data to 100 wt %, using only the oxides Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, CaO, TiO_2, Fe_2O_3, and chlorine. The MgO levels for most

48. S. Cagno and others, “Evidence of Early Medieval Soda Ash Glass in the Archaeological Site of San Genesio (Tuscany),” *Journal of Archaeological Science*, v. 39, no. 5, May 2012, pp. 1540–1552.
49. Coutinho and others [note 19].
50. *Ibid.*
51. *Ibid.*; De Raedt and others [note 36].



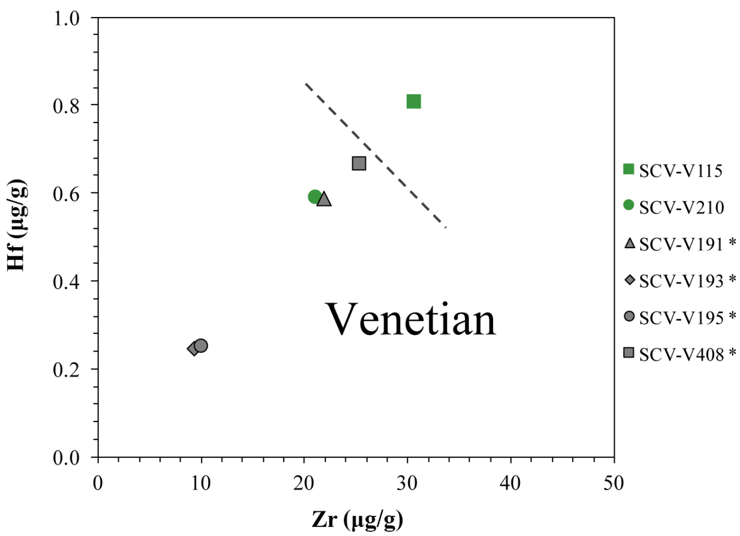


FIG. 6. (Above) *Contents of some trace and rare-earth elements, normalized to Earth's upper crust, for the low-alumina gourds SCV-V115 and SCV-V210, compared with genuine Venetian glasses from the SCV assemblage (Coutinho and others [note 19]), in logarithmic scale;* (left) *binary plot of zirconium vs. hafnium concentrations in µg/g, determined by LA-ICP-MS, for the SCV gourds. The line of dashes refers to the general Venetian regions reported in the literature (De Raedt and others [note 36]).*

of the gourds are above 2 wt %, indicating that ashes from halophytic plants were employed in the glass batch.[52]

In studying the values for potassium and calcium oxides (Fig. 7a), we see that, with the exception of SCV-V177, SCV-V352, and SCV-V365, the gourds are closely related, which might suggest that even the glasses with lower alumina contents can be related to the other objects in terms of the raw material used as the flux, with these two oxides coming from the alkali-rich plant ashes employed in the batch. It seems that the plant ashes used in the batches of the analyzed gourds were collected from the same region, reflecting the similarity in CaO and K_2O contents. SCV-V352 and SCV-V365 appear to be related both in Figure 7a and in the rest of the charts.

The SJT gourd seems to be related to the SCV gourds that contain high and very high alumina, suggesting that these gourds came from the same raw materials and possibly the same location.

In Figure 7b, the fractions of Na_2O and K_2O have been normalized to the content of all alkaline and alkaline-earth oxides.[53] The two lines

52. Šmit and others [note 38].
53. *Ibid.*; Cagno and others [note 48].

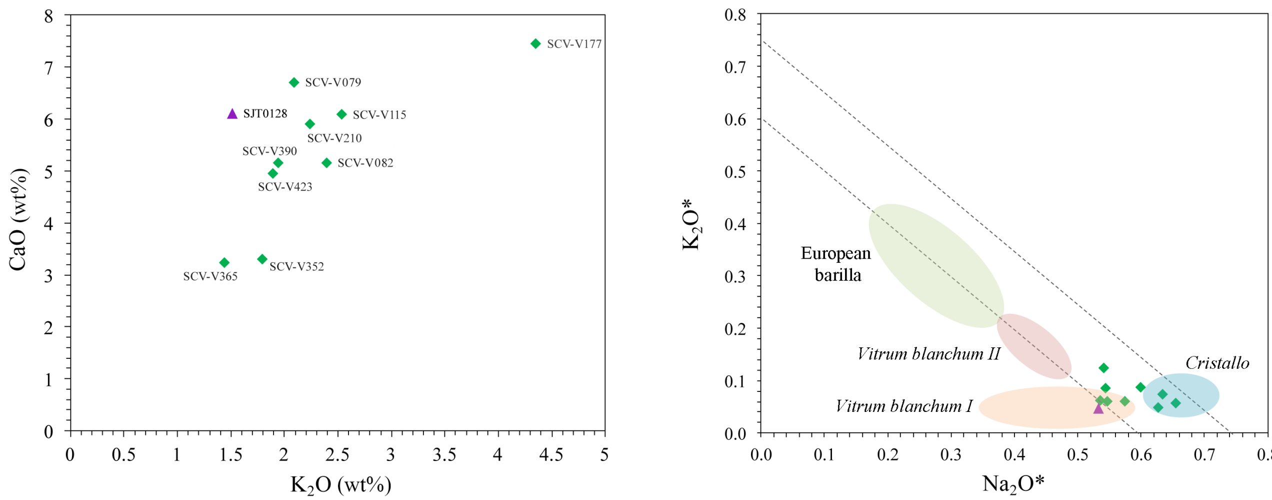


FIG. 7. (Left) *Binary plot of CaO vs.* K_2O *in weight percent of oxides, measured by μ-PIXE;* (right) *binary plot of* Na_2O^* *vs.* K_2O^*. Na_2O^* *and* K_2O^* *values were obtained through the division of the respective oxides by every component introduced by the ash (*Na_2O*, MgO,* P_2O_5*,* K_2O*, and CaO). The two correlation lines represent the purified ash (*$Na_2O^* + K_2O^* = 0.75$*) and the unpurified ash (*$Na_2O^* + K_2O^* = 0.6$*). The Venetian* cristallo *boundaries can be seen, as well as the two* vitrum blanchum *areas and the European barilla area.*

of dashes represent the use of unpurified ashes (correlation line of $Na_2O^* + K_2O^* = 0.6$) and purified ashes ($Na_2O^* + K_2O^* = 0.75$).[54]

A large group of fragments arrange themselves along the inverse correlation line of glass made using unpurified ashes and are close to or within the *vitrum blanchum* boundaries. This does not mean that these gourds are *vitrum blanchum*, but we can nevertheless conclude that most of the gourds were made using untreated ashes from plants rich in sodium. SCV-V115, SCV-V210, SCV-V352, and SCV-V365 appear very close to the *cristallo* boundaries, suggesting that they were made with the purified ashes of sodium-rich plants. Relating this information to what was discussed above concerning the silica and its trace elements, we suspected that SCV-V210 was similar to Venetian glass of the *cristallo* type.

The most remarkable conclusion to be drawn from Figure 7b is that, for this group of gourds, two different manufacturing techniques can be identified, one with purified ashes and the other with unpurified ashes. This reinforces the idea that gourds were produced in more than one location by glassmakers who employed different ways of preparing the raw materials that were introduced into the batch. However, this distinction could also be explained by the use of imported or recycled Venetian glass.

A Colorful Glass

What is immediately striking about the gourd-shaped bottles found in Portugal is the palette used in making these objects. The presence of a certain color in the glass can be attributed to contaminants that have been introduced unintentionally into the batch. This is commonly referred to as “natural coloration” or a “natural hue.” This is the case with iron oxide, for example, the presence of which is generally attributed to the raw material used for silica. There are some instances in which the coloration is considered intentional, and this is the case for

54. Cagno and others [note 48].

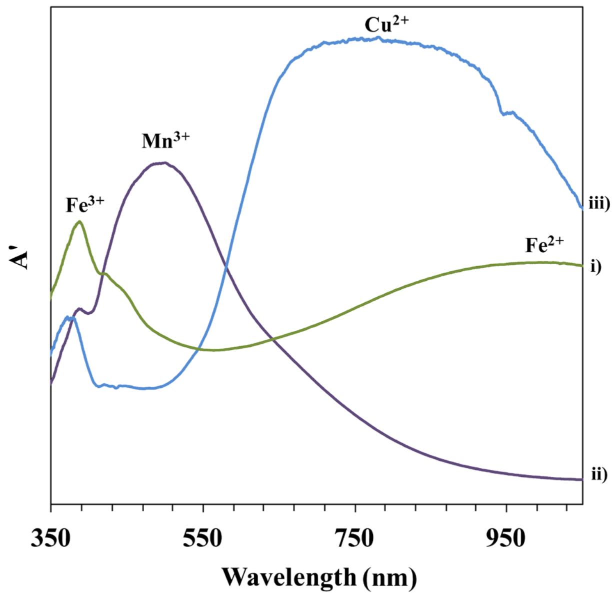


FIG. 8. *UV-Vis absorbance spectrum of (i) SCV-V365, green; (ii) SCV-V82, purple; and (iii) SCV-V210, turquoise blue.*

cobalt blue. The cobalt in the glass matrix is considered to have been added deliberately, as was also true for the purple glass, rich in manganese oxide. Considering the intense coloration of most of the recovered vessels, we can suggest that the glassmakers purposely used glass that they knew would result in bright, colorful objects.

We can see that, in Table 1, the most common color among the sampled objects (in five of the 10 gourds) is green, and this is also reflected among the total number of gourds found to date (67 out of 133).[55] The results for spectrum i) in Figure 8 allow us to identify the presence of octahedral Fe(II), with a broad band centered around 1100 nm, and tetrahedral Fe(III), by its typical absorption bands at 380 and 420 nm, as responsible for the green color. The presence of iron is generally considered to be an impurity typically attributed to the silica source. Looking at the green tints in the SCV set, we can debate the intentionality of the presence of iron. It is important to clarify what is meant here by intentional: (a) iron can be added on purpose to obtain the green color, (b) glassmakers purposely used sands rich in iron to obtain green glass, and (c) sands rich in iron were used on purpose, to which manganese was added, not to decolorize but to enhance the green color in the glass.

The concentration of MnO in the glass seems to suggest that this component was introduced into the batch deliberately, pointing to the hypothesis described in (c). In Figure 9, the contents of Al_2O_3, SiO_2, TiO_2, MnO, and Fe_2O_3 were normalized to muds of Queensland (MUQ) concentrations because these values are a good approximation to the weathered continental crust, for instance clay.[56] Looking at the pattern of these oxides, especially that of MnO, which should behave similarly to iron, we would expect MnO to present a concentration similar to Fe_2O_3 (after both were normalized to MUQ). We can see in Figure 9 that, for the majority of the gourds, MnO is in a much higher concentration than the rest of the plotted oxides, which reinforces the hypothesis of a deliberate addition of manganese to the glass.

We propose that manganese was not added to discolor the batch; instead, it may have been introduced as recycled cullet. The other suggestion is that, because MnO_2 (the form in which manganese is added to the batch) has an oxidizing effect, it was probably introduced into the batch to counteract the strong blue coloration provided by the reduced iron. In this way, manganese would oxidize the iron to a green color.

Only one gourd of purple glass (SCV-V082) was sampled, although that color is widely represented in the archaeological assemblage from the Monastery of Santa Clara-a-Velha (48 examples). This color is dark, and it seems to be almost black in the thicker areas of the glass. It is considered to be intentional, with the deliberate addition of manganese to the batch having been necessary to achieve it. In SCV-V082, the

55. See Medici, "Vidros da Terra," [note 1], v. 2.

56. Balz S. Kamber, Alan Greig, and Kenneth D. Collerson, "A New Estimate for the Composition of Weathered Young Upper Continental Crust from Alluvial Sediments, Queensland, Australia," *Geochimica et Cosmochimica Acta*, v. 69, no. 4, 2005, pp. 1041–1058; Ian Freestone, personal communication.

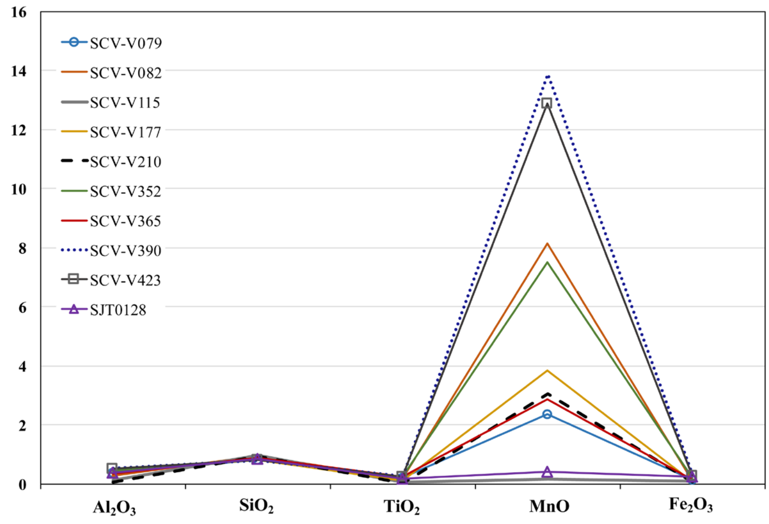


FIG. 9. *Contents of some elements related to the silica source employed in the glass gourds, normalized to MUQ (muds of Queensland).*

presence of Mn(III) was identified by UV-Vis reflectance spectroscopy (Fig. 8, spectrum ii) as the main chromophore, characterized by an absorption band between 450 and 500 nm.[57] This broad band masks the presence of Fe(III), but iron can be identified through the chemical analysis by μ-PIXE and LA-ICP-MS (Table 1).

Finally, SCV-V115 and SCV-V210 are made of blue glass. One of these gourds is very light blue, while the other is a strong turquoise blue. In the case of SCV-V115, the blue color is due to the presence of Fe(II) and some Fe(III). The turquoise color of SCV-V210 is due to copper (Cu^{2+}), characterized by a broad band around 790 nm, and Fe(III), as can be seen in Figure 8, spectrum iii). Thirty blue gourds have been recovered from the excavation of the monastery.

CONCLUSIONS

This study came about because previous investigations had shown that gourd-shaped glass bottles were repeatedly found in Portugal, but not extensively in the rest of Europe.[58] For the first time, a set of gourd-shaped bottles has been chemically characterized, and its composition has been compared both with that of contemporaneous glasses from known European production centers and with that of *façon de Venise* glass of similar date found in Portugal. The analyzed vessels came from archaeological excavations at two monastery sites, and most of them have similar chemical compositions, mainly in terms of their silica source. In general, they are high in alumina (> 6 wt %), which reinforces the hypothesis that these objects were produced in Portugal, using sources of silica that were less pure and rich in feldspar, as has been noted in previous works on glass found in Portugal.[59]

Two of the 10 analyzed gourds have low levels of alumina, which suggests the use of a purer silica source. It was determined that the composition of one of these gourds (SCV-V210) was compatible with that of Venetian glass. This allowed us to suggest that the gourd was either produced in a Venetian workshop or made elsewhere with recycled Venetian glass. The analysis of major and minor components of the glass,

57. Rossella Arletti and others, "Florence Baptistery: Chemical and Mineralogical Investigation of Glass Mosaic Tesserae," *Journal of Archaeological Science*, v. 38, no. 1, January 2011, pp. 79–88.
58. Medici [note 1], pp. 273–275.
59. Coutinho and others [note 19]; Lima and others [note 35].

as well as the uniqueness of the shape, led us to conclude that the second suggestion was more likely to be correct.

In terms of fluxing agents, we were able to distinguish two different manufacturing techniques: one using purified ashes and the other employing unpurified ashes. Moreover, the heterogeneities observed in the compositions could mean that several glass production centers, probably located in the same region or sharing the use of a similar siliceous raw material, were involved in making these vessels.

The shape of these vessels is rare in other European glass production centers of comparable date, and the results of the chemical analyses support—or at least do not contradict—the idea that the gourds were probably produced in Portugal. It should not be by chance that, among the infrequent representations of glassware in 17th-century Portuguese paintings, an unambiguous colorless gourd appears in a work by Josefa de Óbidos.

The assumption of Portuguese production suggests that skilled glassmakers were working in Portugal in the early modern period. This calls into question the commonly accepted notion that glass made in Portugal at that time was of poor quality, crafted by less capable artisans. On the contrary, the results of our study reinforce the impression that local production should have attained some significance, at least from the 16th century onward. This seems to be implied in an existing royal charter from King Dom Sebastian I (1554–1578), dated 1563, which appears to have forbidden the importation of Venetian glass because local production was judged to be of comparable quality.[60]

The lack of archaeological data on glass furnaces dated to the early modern period, which would allow us to analyze the remains of glass production and better attest provenance, creates difficulties in declaring glass to have been produced in Portugal. It would be interesting to analyze raw materials (especially sand) from certain locations where glass objects of this period have been found. In this way, we could compare the analytical data from both the objects and the raw materials, and perhaps speculate more strongly about the provenance of the gourds. The suggested link between the gourds and the Islamic glass repertoire is another aspect of this subject that requires further investigation.

I. Coutinho
Research Unit VICARTE (Vidro e Cerâmica para as Artes)[a]
and *Department of Conservation and Restoration*[b]
Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa, Campus de Caparica
2829-516 Caparica, Portugal
iac17191@campus.fct.unl.pt

T. Medici[a]

R. Wiley[a]

L. C. Alves
C2TN, Instituto Superior Técnico
Universidade de Lisboa, E.N.10
2695-066 Bobadela LRS, Portugal

B. Gratuze
IRAMAT – Centre Ernest-Babelon
CNRS Université d'Orléans
45071 Orléans Cedex 2, France

M. Vilarigues[a,b]

60. Teresa Medici and others, "Looking through Late Medieval and Early Modern Glass in Portugal," *Annales de l'Association Internationale pour l'Histoire du Verre*, v. 20, Fribourg, 2015, forthcoming.